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## **I. Abstract**

During the term of this research grant, design and construction of a state-of-the-art surface science apparatus was performed. In particular, an apparatus was built which is capable of addressing the issues unique to wide bandgap semiconductor surfaces and their processing into electronic devices. The superlative properties of these materials are accompanied by considerable challenges in their investigation. Among the design requirements established for this chamber were the ability to heat to a temperature of 1050° C, the ability of to employ novel cleaning techniques without contaminating analysis equipment, and the ability to detect and characterize surface hydrogen. The apparatus design meets these constraints through the use of an electron beam sample heater, a high-temperature sample mounting puck, an interchamber sample translation system, a dedicated surface preparation chamber, and the best performance high resolution electron energy loss spectrometer available. With construction nearly complete, a research program investigating surface processes critical to the use of wide bandgap semiconductors in electronic devices is being initiated.

## **II. Research Goals**

The overall goal of the research program which is being established in the research group of Dr. Brian Thoms is to develop a fundamental understanding of wide bandgap semiconductor surfaces while paying special attention to those properties of the surfaces which impact the application of these materials in electronic devices. For the near future, the focus of the work will be diamond and the wide bandgap nitrides, AlN and GaN. In particular, two research areas have been identified. The first is an investigation of the role of surface hydrogen in the growth and modification of these materials. Hydrogen has already been shown to be critical to the structure and reactivity of the surfaces of narrow bandgap semiconductors and diamond and we have suggested that it will play a similarly critical role for the nitrides. Hydrogen incorporation into growing nitride films is also of great importance. Hydrogen incorporated into the bulk and forming complexes with dopants during the growth of GaN is believed to cause deleterious effects on the electrical characteristics. The second research area we have identified is the etching of wide bandgap nitride surfaces. Etching steps are used in processing semiconductor materials into devices, however, etching of these materials has proved difficult and almost nothing is known about the fundamental surface processes occurring during etching.

## **III. Design Requirements**

These research goals for both the overall program and the initial areas of investigation lead to a number of design considerations which were incorporated into the apparatus.

Wide bandgap semiconductors are typically grown at high temperatures. These high temperatures are necessary because of large energy barriers for diffusion and for making and breaking bonds in the bulk as well as on the surface. GaN is typically grown at temperatures near 1000° C. Surface modification processes, e.g. etching, might also be expected to require higher than usual temperatures. All of the reported techniques for preparation of clean surfaces involve heating to temperatures near 1000° C. For this reason design requirement for the capability to heat the sample to 1050° C was adopted.

In order to investigate well-characterized surfaces, the sample must be cleaned of undesired adsorbates and prepared in a controlled and reproducible state, preferably similar to that which might

occur during growth or processing. Clean, smooth, well-ordered, diamond surfaces can be produced by exposure to large fluxes of hydrogen atoms while the diamond is at elevated temperatures. In the case of AlN, no successful techniques for surface cleaning in vacuum have been reported due to the extremely stable oxide which forms when AlN is exposed to air. Previous researchers have instead grown a thin AlN film *in situ* in order to obtain the necessary cleanliness and reproducibility. GaN has been grown *in situ*, but it has also been successfully cleaned using several procedures. These include exposure to Ga from an evaporator, nitrogen ion bombardment, and exposure to ammonia gas. Each of these cleaning procedures requires a high temperature anneal to produce a reproducibly clean surface. It is not clear which of these procedures results in the best surface for subsequent surface science experiments. Unfortunately, these surface preparation procedures could result in contamination of sensitive analytical equipment or vacuum chambers. Therefore, a design requirement of a dedicated sample preparation chamber and interchamber sample translation was adopted.

Once the sample has been cleaned, background gas from the chamber will strike the surface and create contamination. In order to maintain a clean surface for a sufficient period of time to perform experiments, the vacuum system must achieve very low background pressures. Our design criterium was that the analytical chambers must achieve base pressures less than  $2 \times 10^{-10}$  Torr. This design consideration requires vacuum pumps with base pressures below  $2 \times 10^{-10}$  Torr and that all nonremovable pieces of the apparatus be capable of withstanding a bake-out of  $>150^\circ \text{C}$ .

The clean sample must be characterized to demonstrate that the starting point for each experiment is a reproducible sample surface. Typical characterization tools are Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). AES is used to characterize surface composition and bonding while LEED is used to characterize surface order. A requirement for our chamber to accommodate these analytical tools was also adopted. These techniques can be used for more than just assuring reproducible initial surfaces. They are also valuable tools for characterizing the effects of surface processes. AES will be extremely useful for quantifying surface adsorbates (for instance, etchants) and quantifying changes in surface stoichiometry. LEED will detect changes in surface ordering. Both techniques use low energy electrons and are, therefore, sensitive only to the near surface region.

The role of hydrogen in surface processes is one of the research areas we will investigate. The emphasis on hydrogen results in a requirement for an analytical technique which can detect and characterize surface hydrogen and surface species containing hydrogen. Neither AES or LEED can directly detect surface hydrogen. In addition, to fully understand hydrogen's role in surface processes requires a method to identify molecular species containing hydrogen which might be liberated into the gas phase. The technique chosen to detect surface hydrogen was high resolution electron energy loss spectroscopy (HREELS) and the device chosen to detect gas phase species was a quadrupole mass spectrometer (QMS). HREELS is a surface sensitive vibrational spectroscopy which identifies surface species and their bonding environment by their vibrational frequency. A QMS can be used in many ways to detect gas phase species. One of these is temperature programmed desorption (TPD) in which the sample temperature is increased linearly and the species which desorb from the surface at each temperature are detected by the QMS. Our apparatus design was therefore constrained to accommodate a HREEL spectrometer and differentially pumped QMS. The sensitivity of the HREEL spectrometer to contamination resulted in an additional design constraint of housing that instrument in a chamber which can be isolated from any gas exposure during dosing or sample heating.

#### **IV. Apparatus Design**

The final apparatus design contains three connected ultrahigh vacuum chambers as shown in the system overview in Fig. 1. All the vacuum chambers were manufactured by the Kurt J. Lesker Company. The lowermost chamber contains the HREEL spectrometer and is evacuated by a Perkin Elmer 220 l/s ion pump. The ion pump also performs pressure measurement for the lower chamber. Since the HREEL spectrometer is the most powerful of the analytical tools comprising this system and since the planned experiments will require the distinguishing species with similar vibrational frequencies, the highest resolution spectrometer presently available was chosen. This spectrometer, designed by H. Ibach and group in Julich, Germany and manufactured by LK Technologies is capable of a resolution of 1 meV ( $8\text{ cm}^{-1}$ ). The chamber is designed specifically to accommodate the HREEL spectrometer and has two layers of magnetic shielding inside as shown in Fig. 2. The sample is lowered into the spectrometer from above.

An upper chamber is attached to the topmost flange of the spectrometer chamber via an intervening gate valve. This valve allows the spectrometer chamber to be isolated while the sample is heated or exposed to gas in the upper chamber, thereby keeping the spectrometer free of contaminants. The upper chamber has a total of fourteen ports and is shown in Fig. 3. The upper chamber is evacuated by a Balzers 200 l/s turbomolecular pump which is backed by a Edwards two-stage mechanical pump. Two of the ports were designed to accommodate LEED and AES devices. Due to budgetary considerations, the system is presently equipped with a combination LEED/AES device manufactured by Omicron. This device acquires AES spectra using the retarding field method and achieves somewhat poorer energy resolutions than what is achieved with the more common cylindrical mirror analyzers (CMA). The quality of the LEED data acquired is not compromised by the incorporation of AES capabilities. A separate port is designed to accommodate a CMA for a future performance upgrade. A differentially pumped QMS is presently being added to the upper chamber and will be capable of performing TPD experiments. The upper chamber also houses an ion gauge for pressure measurement, variable leak valve for gas dosing, tungsten filament for hydrogen atom creation, and glass viewports. The sample manipulator attaches to the topmost flange of the upper chamber. The manipulator is an Omniax manufactured by the Kurt J. Lesker Company. It allows full 360° rotation, one inch of travel in the horizontal plane for positioning, and 24" of vertical travel. With this range of motion the sample can be moved to face any of the ports in the upper chamber and its position adjusted for optimum performance of the analytical techniques. The sample can also be lowered through the gate valve into the spectrometer chamber where it can be positioned for acquisition of HREEL spectra.

The sample preparation chamber is connected to one of the side ports of the upper chamber by a gate valve. This small chamber, shown in Fig. 4, is evacuated by a Balzers 65 l/s turbomolecular pump which is backed by a Balzers diaphragm pump. This chamber is equipped with an ion gauge, gas dosing connections, viewports, and sample cleaning devices such as an ion gun or Ga evaporator. The sample is mounted on a removable puck which can be transported between the sample preparation chamber and the upper chamber on a magnetically coupled linear transfer arm. Once in the sample preparation chamber, the puck is mounted onto a manipulator equipped with 360° of rotation and 2" of vertical travel. This vertical travel is required so that the

end of the manipulator can be raised out of the way when the linear transfer arm is retrieving the sample from the upper chamber. Sample cleaning can be performed in this chamber while the upper and lower chambers (housing the surface analytical equipment) remain under ultrahigh vacuum.

The sample puck is a removable sample mounting stage and is shown in Fig. 5. This stage is made almost entirely of tantalum so that the sample mount can withstand high temperatures. The sample itself is mounted onto a small tantalum plate which is heated from behind by electron bombardment. This small "hot plate" will get considerably hotter than all other parts of the sample mount. The hot plate is attached to the rest of the puck by ceramic screws and sapphire balls, providing electrical isolation but allowing some heat transfer to occur for adequate cooling. Three wires are connected from the hot plate to posts on the puck, two comprise a thermocouple while the third provides electrical bias or grounding of the hot plate. The heating stage, which is rigidly connected to the sample manipulator, accepts the puck by receiving these posts and their associated ceramic housings making the electrical and mechanical connections between the puck and the heating stage. The heating stage is constructed of OFHC copper to dissipate heat efficiently and is shown in Fig. 6. This stage holds the electron beam heater (a tungsten filament in a ceramic sleeve). It also houses the sockets into which the posts on the puck insert making the electrical connections. These sockets and the heater filament are attached to wires which run up the shaft of the manipulator to feedthroughs at the top of the manipulator. Liquid nitrogen cooling will be added in the future using a liquid feedthrough at the top of the manipulator, a small stainless steel tube ending at a copper block, and copper braid for heat transfer. All pieces of the sample mount within 4" of the sample are nonmagnetic. The only magnetic material which will be inside the magnetic shielding during operation of the HREEL spectrometer is the stainless steel shaft of the sample manipulator which should have a negligible residual magnetism.

## **V. Construction**

The surface science apparatus constructed during the term of this ONR grant was funded by university start-up funding, additional departmental support, and Georgia State University Equipment Matching Program and Quality Improvement Program funding in addition to the ONR funding. All major equipment has been purchased except for the Quadrapole Mass Spectrometer and



its differential pumping. These items are being purchased with recently awarded funds from the Georgia State University Quality Improvement Program.

Assembly of the apparatus is nearing completion. All vacuum chambers and pumps have been assembled and the system has achieved a base pressure of  $2 \times 10^{-10}$  Torr. The HREEL spectrometer has been installed and tested. The LEED/AES device has also been installed and tested. Assembly of the sample manipulator including heating stage and sample puck is nearing completion. Testing of the sample heating and puck transfer system will follow installation of the completed sample manipulator.

First data collection is presently expected to occur in February of 1997.

## **VI. Planned Research**

As described in the Research Goals portion of this report, the two areas of initial research are an investigation of the role of surface hydrogen in the growth and modification of wide bandgap semiconductors and the etching of GaN and AlN.

Initial experiments will be investigations of the interaction of hydrogen on a diamond C(100) surface. This system has been chosen as a starting point since the principal investigator has considerable knowledge and experience with this system. That should allow testing of the apparatus and any necessary modifications to proceed rapidly.

Once the system is shown to be working as designed, GaN samples will be obtained from researchers at the Naval Research Laboratory in Washington, DC. The first step in the GaN research will be development of an experimental procedure to achieve clean, well-ordered surfaces in our system. Nitrogen ion bombardment followed by vacuum annealing will be the cleaning method used. Characterization of the clean GaN surface will be made using LEED to determine surface order and AES to determine stoichiometry and to check for contamination. Some characterization of clean GaN surfaces has previously been done by other researchers.

Once clean GaN is achieved, HREEL spectra will be taken. These data should reveal details of the structure of the clean surface. Earlier research in other laboratories has suggested that hydrogen is present on the GaN surface even after cleaning, however, those experiments could not make a conclusive determination. Our HREEL spectra will conclusively identify any surface

hydrogen and its bonding configuration ( $\text{GaH}$ ,  $\text{GaH}_2$ ,  $\text{NH}$ ,  $\text{NH}_2$ ).

The clean GaN surface will then be exposed to various amounts of molecular or atomic hydrogen. LEED will be used to observe any changes in surface structure that result from these exposures. HREELS will determine whether the hydrogen adsorbs onto the surface and identify its bonding sites. The effects of temperature on the hydrogenated surface will be examined in several ways. First, a series of anneal and quench experiments will attempt to observe changes in surface structure and hydrogen bonding configuration as a function of annealing temperature. Second, TPD experiments will be used to determine whether hydrogen desorbs from the surface, in what form it desorbs (hydrogen molecule, ammonia, gallium hydride), and the kinetics of that desorption. Hydrogen is abundant in the environment which is used to grow GaN and removal of surface hydrogen may be a critical step in the growth. Hydrogen removal may also be critical to processing of these materials into electronic devices. For instance, it might be expected that surface hydrogen has a role in metallization and influences the quality of the contact produced.

The reaction of chlorine on the GaN surface would be expected to be similar to the reaction of hydrogen. Chlorine has been used in nearly all attempts at GaN etching to date. This is due to the success of chlorine-based etching processes for GaAs. The experimental procedures for investigating the reaction of chlorine with the GaN surface will be very similar to those used for hydrogen. Clean GaN surfaces will be exposed to various amounts of molecular or atomic chlorine. LEED will be used to detect changes in surface structure while HREELS will be used to identify chlorine adsorption and bonding configuration. HREELS and LEED observations as a function of annealing temperature will reveal the initial steps of the etching reaction. TPD experiments will detect the etch products as they leave the surface. HREELS and LEED following TPD will show the surface structure which is created by the etching reaction. AES may be used to measure surface chlorine at various stages of the process, however, the accuracy of these measurements must be tested since chlorine has a very high cross-section for electron stimulated desorption.

These initial experiments will undoubtedly suggest many other relevant avenues of research. One future avenue was outlined in the research proposal, that is, the use of non-thermal processing (electrons and photons) to modify the surface of wide bandgap surfaces in a spatially selective fashion.

## VII. Conclusion

Research on wide bandgap nitrides has enjoyed a surge in activity in recent years due to advances in materials growth and in the development of blue-light emitting devices. Beyond this recent activity is the promise of better high-power, high-frequency electronics. Achieving this second goal will require progress in several significant areas of processing technology which can be advanced through surface science research.

Under this research grant, a state-of-the-art surface science apparatus has been designed and constructed. This apparatus addresses the unique properties of wide bandgap semiconductors. With these unique properties comes unique possibilities, as well as unique challenges. The construction of this apparatus is a step toward meeting those challenges.

Among the research areas which will be investigated with this apparatus are;

- \* identification of the structure of clean and hydrogenated GaN surfaces,
- \* determination of the kinetic parameters for thermal hydrogen removal from GaN,
- \* identification of the mechanism by which chlorine etches GaN,
- \* determination of the kinetic parameters of the etching of GaN with chlorine,
- \* investigation of novel etching techniques for GaN and AlN, and
- \* investigation into the use of electron and photon processing of GaN and AlN.

Figure 1 System Overview

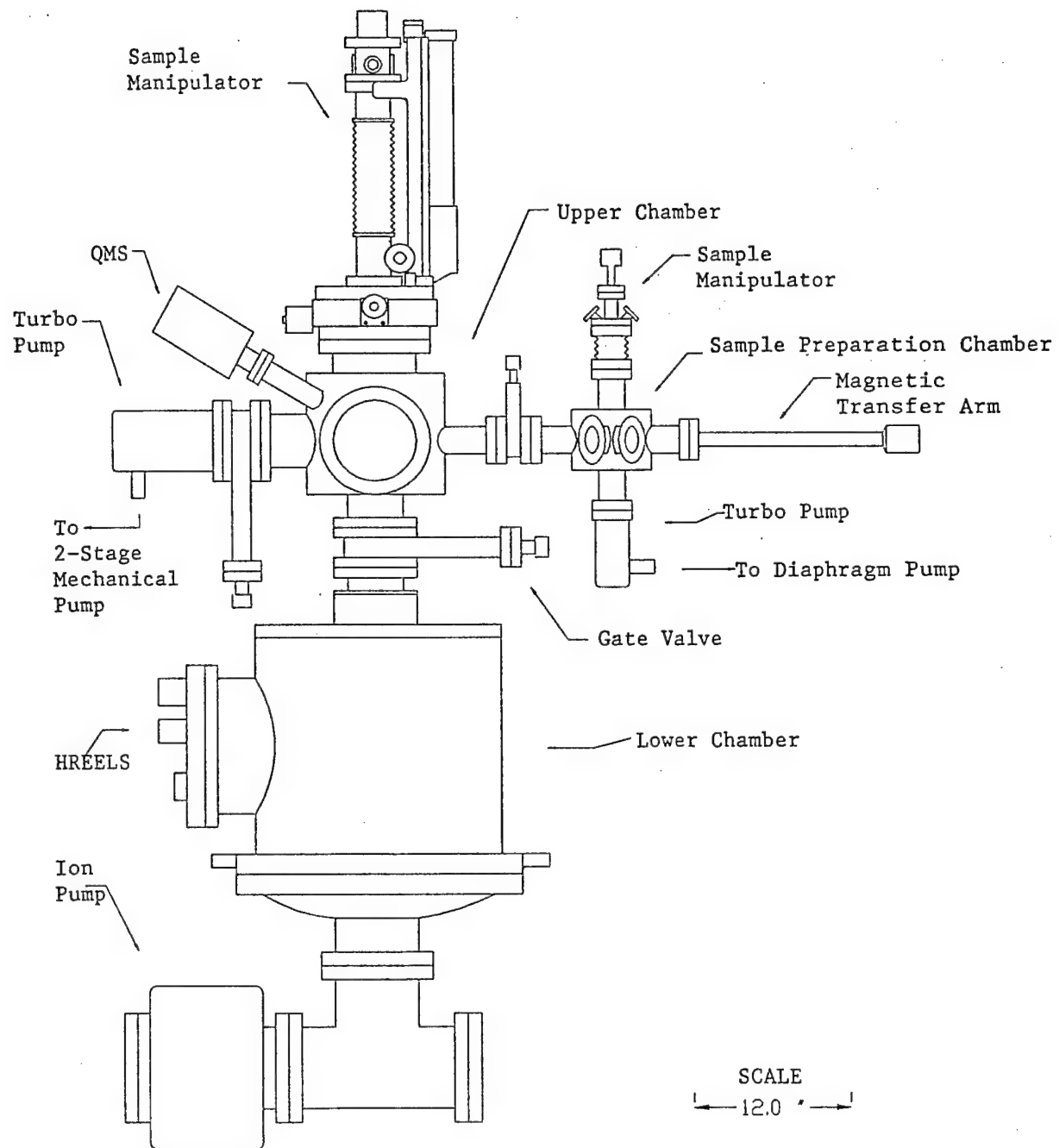
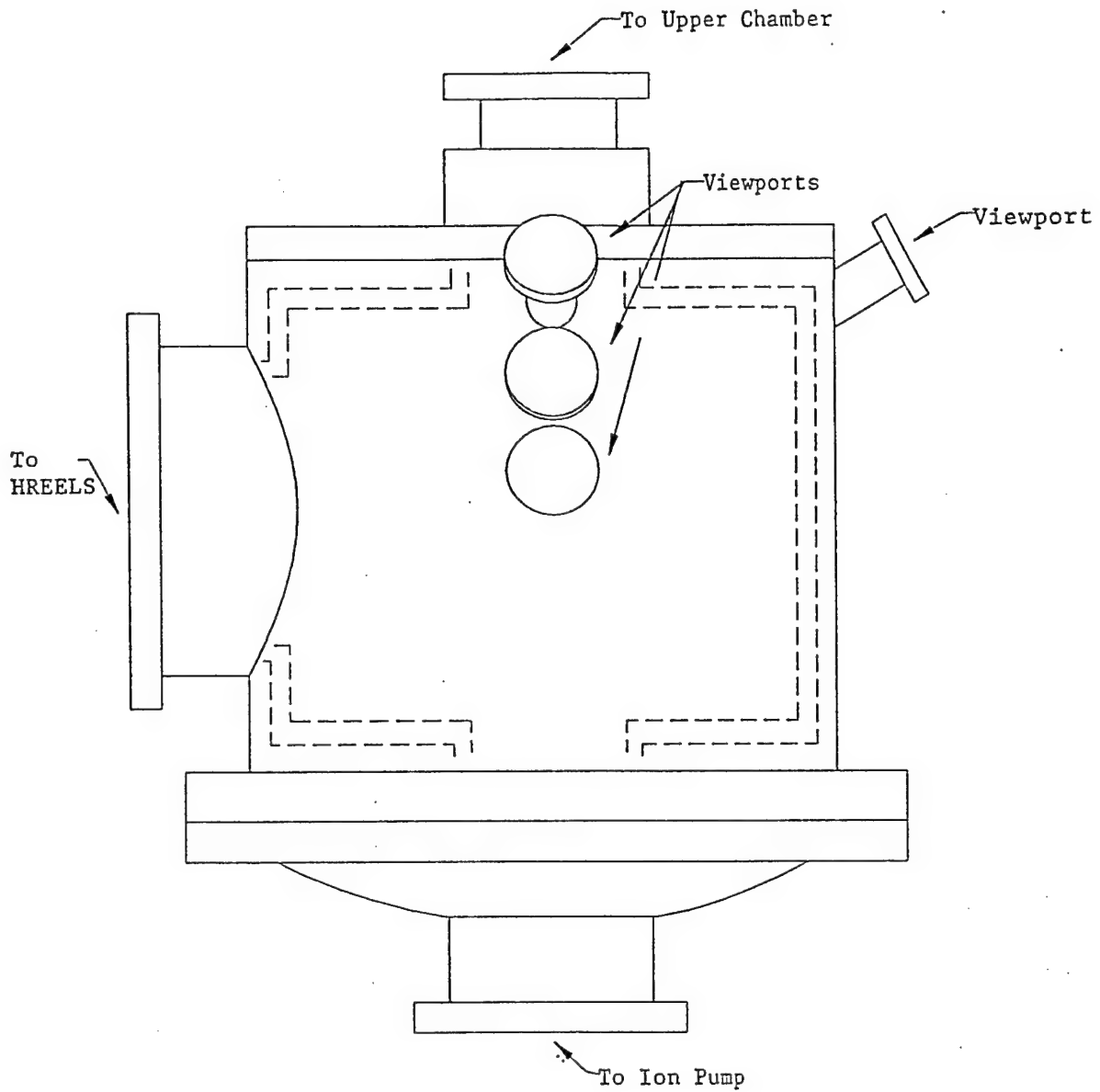


Figure 2 Lower Chamber



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12.0 "

Note: Dashed lines represent magnetic shielding

Figure 3 Upper Chamber

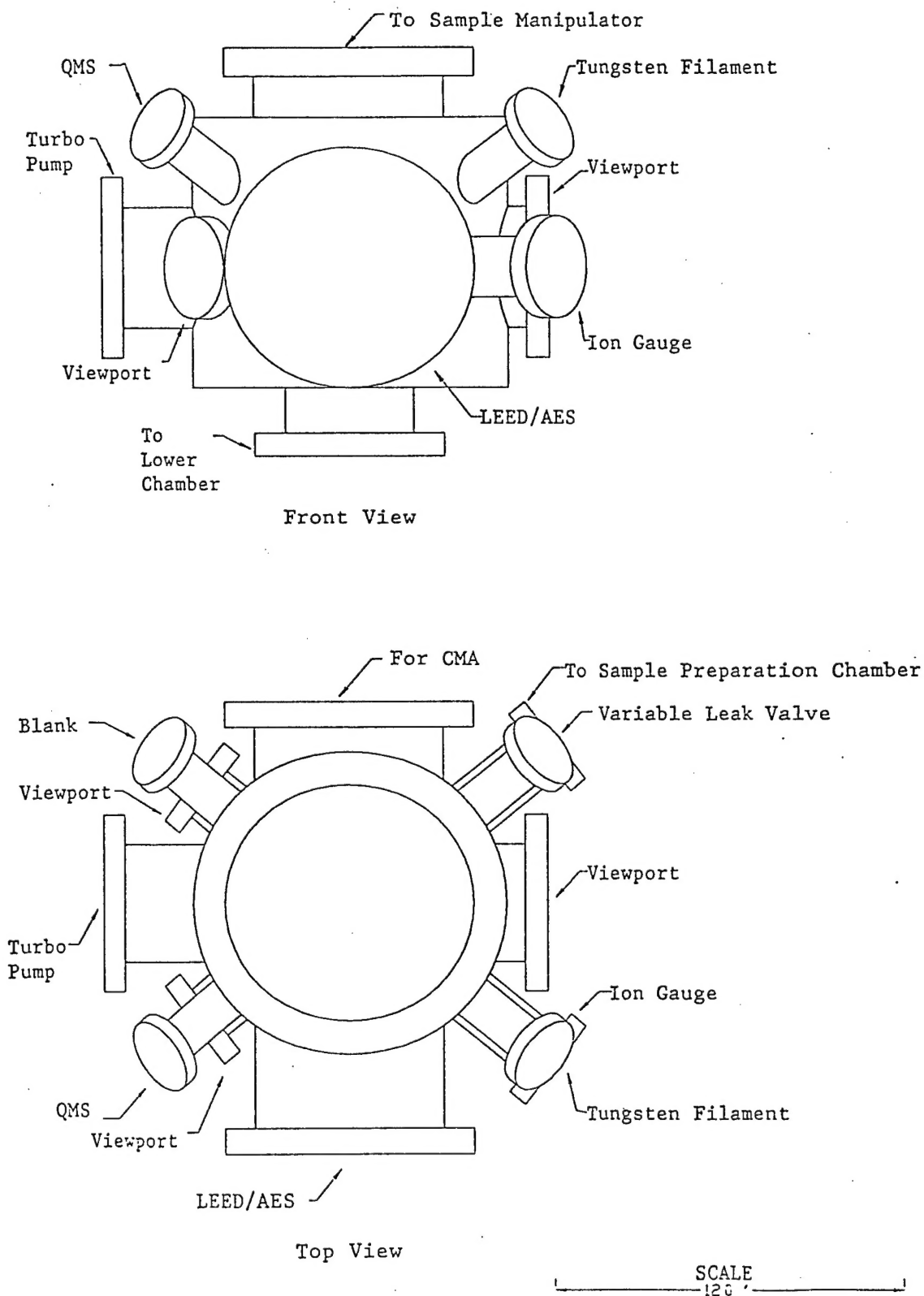


Figure 4 Sample Preparation Chamber

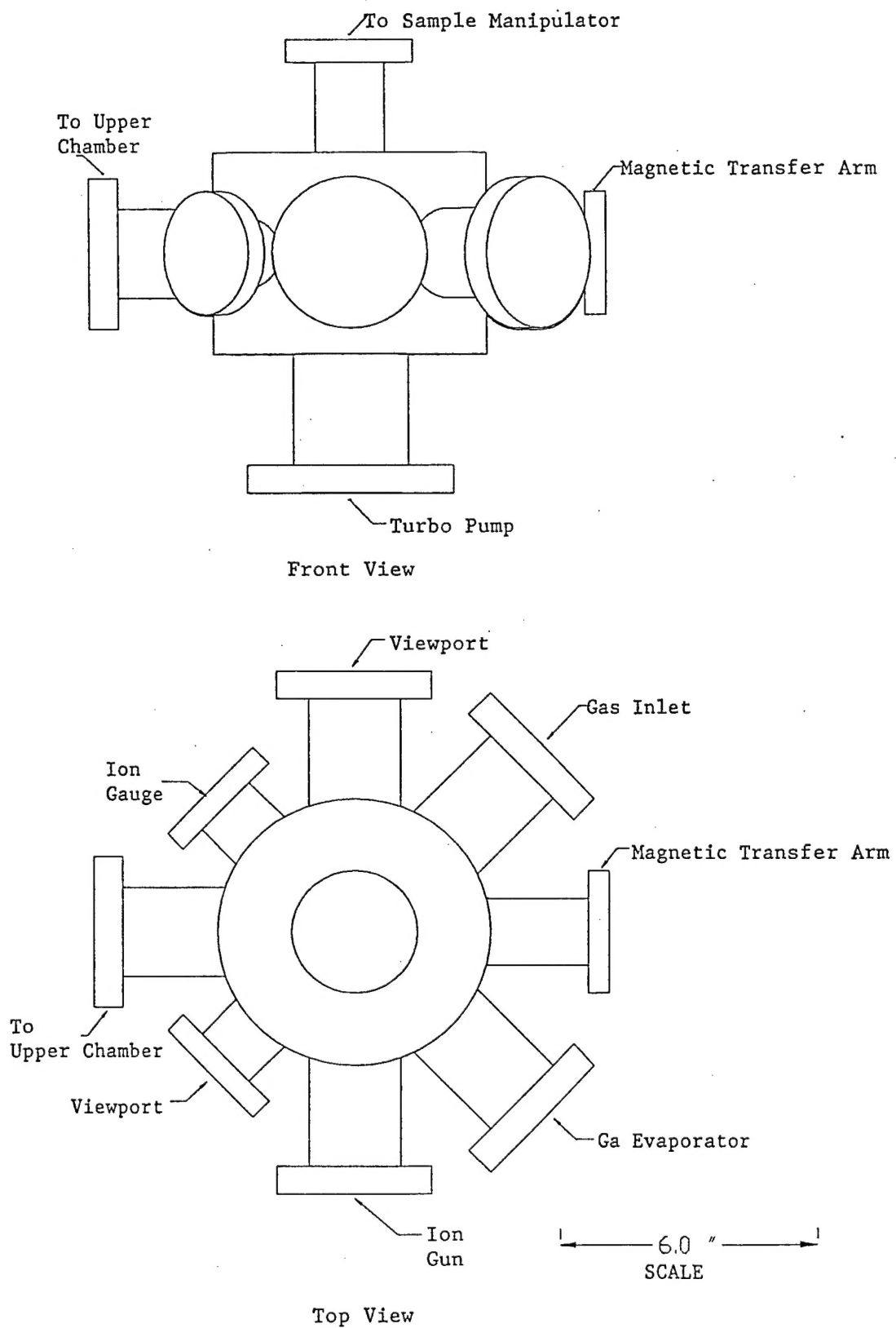


Figure 5 Sample Puck

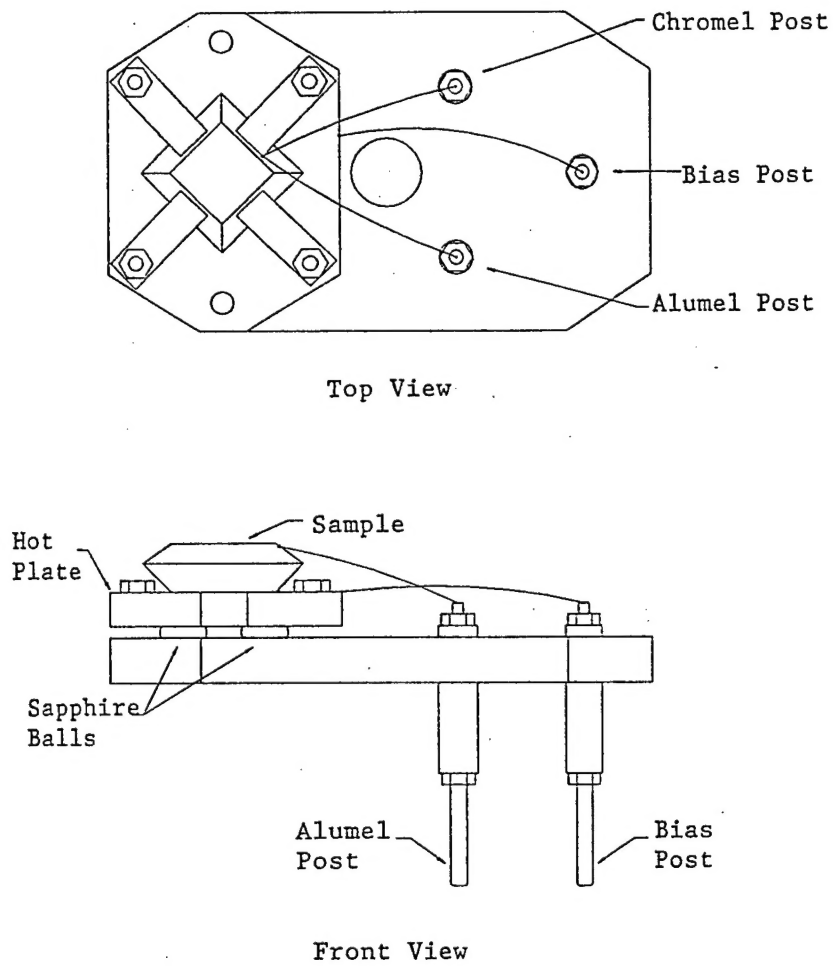
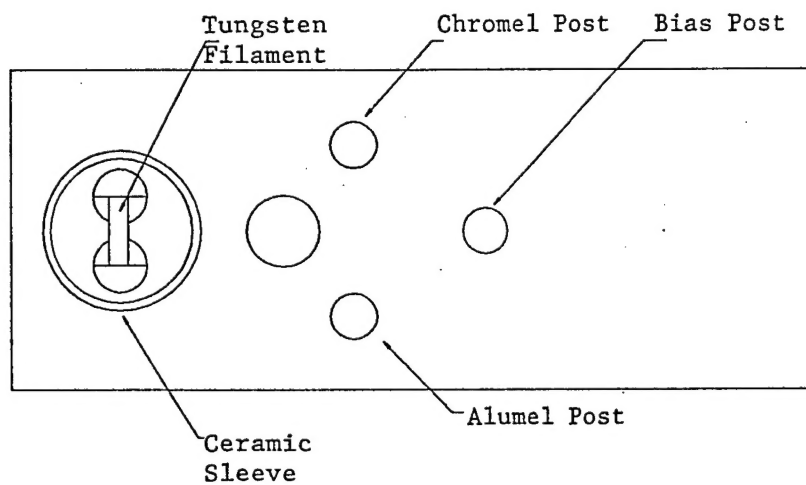
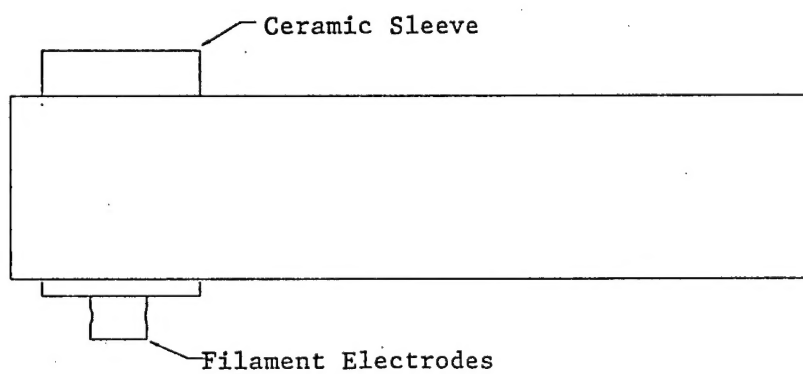




Figure 6 Heating Stage



Top View



Front View

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